2. Potassium and chloride in soils

2.1. Sources of potassium and chloride

2.1.1. Source of soil potassium

Potassium is present in igneous, sedimentary, and metamorphic rocks and comprises about 25 g kg^{-1} of the earth's crust (Sheldrick, 1985). In mineral soils, K generally ranges between 0.4 and 30 g kg^{-1} (Sparks, 1987) with most agricultural soils containing between 10 and 20 g kg^{-1} (Jackson, 1964; Xie and Hasegawa, 1985). Total K contents in soils generally range between 10,000 and 50,000 kg ha^{-1} in the upper 0.2 m of the soil profile. Of this total K content, about 98% is bound in the mineral form and only about 2% is in the soil solution and exchangeable phases (Sparks, 1987). The K content in a soil is a reflection of its parent material, degree of weathering, and amount of K fertilizer added minus losses due to crop removal, erosion and leaching.

The average K content in igneous rocks (including metamorphic), shale, sandstone and limestone rocks in the lithosphere is in the order of 26, 27, 11, and 2.7 g kg^{-1}, respectively (Bertsch and Thomas, 1985). The most important sources of K in mineral soils are the primary alumino-silicates, K-feldspars, biotite, and muscovite micas. The soils contain their weathering products, the secondary aluminosilicates, comprising the hydrous micas (illite), the vermiculities, smectites, and their hydroxyl-Al interlayer analogues. The K-feldspars comprises approximately 15% of the total lithosphere (Huang, 1977). The relative importance of K-feldspars in relation to K availability is very dependent on the intensity of weathering, time of deposition or exposure and other factors. The K content of the 2:1 phyllosilicate minerals present in most soils ranges from 83 g kg^{-1} for the soil micas to 33 g kg^{-1} for the hydrous micas or illites (Huang, 1977). The structural differences between the various mica minerals are of great significance in determining the ease of weathering and K release characteristics. The potential of K supply to crops is dependent on the intensity of weathering, and the relative composition of the soil minerals. Micaceous minerals and their weathering products are the most important sources of plant available K in any soil system.

2.1.2. Sources of chloride

The sources and concentrations of Cl in nature are listed in Table 2.1. Four basic factors determine the amount of Cl available to crops growing in well-drained soils: (1) the Cl concentration in the soil solution; (2) atmospheric deposition of Cl; (3) the Cl concentration in the irrigation water; and (4) the content of Cl in fertilizers and manure (Goos, 1987). As a result of their genetic characteristics, crops have different requirements for and tolerance to Cl. Therefore, when attempting to establish exact levels of permitted Cl in soils and irrigation water, plant factors should be taken into account.

Table 2.1. Chloride concentrations in some natural sources.

Source	Chloride (g kg^{-1})
Earth crust	1.50
Lithosphere	0.48
Basalt rocks	0.50
Syenite	0.98
Igneous rocks	0.23
Shale	0.16
Sandstone	0.02
Limestone	0.37
Dolomite	0.50
Soils	0.10
Ocean	19.0
Plants	1.0-10.0
Low to medium saline water	0.10-0.30[a]
High to very high saline water	0.30-1.20[a]
Table salt (NaCl)	607
Potassium chloride (KCl)	450-570

Compiled from Yaalon (1963); Flowers (1988).

[a] Unit: kg m^{-3}

2.1.2.1. Soil

The Cl content of the lithosphere is similar to that of S (about 500 mg kg^{-1}) and is slightly less than half of that of P (Flowers, 1988). Chloride is one of the first elements removed from minerals by weathering process as soils are formed. Therefore most of world's Cl is either found in oceans or in salt deposits left by evaporation of old inland seas. Salt marsh soils may contain more than 800 mM (Flowers, 1988). The Cl content of the soil is not an intrinsic property of the soil but is a result of soil management, because of its mobility in the soil and the fact that it moves with the water in the soil.

2.1.2.2. Irrigation and fertilization

The amount of Cl added to a field via the irrigation water (fresh or treated municipal effluents) depends on farm activities. Water of low to medium salinity contains 100-300 g Cl m^{-3} (Table 2.1), whereas saline water contains 300-1200 g Cl m^{-3}.

It is estimated that by the year 2000, the total annual amount of Cl used in fertilizers in China, mainly as NH_4Cl and KCl, will be $5x10^9$ kg (Pan *et al.*, 1991a; Yin *et al.*, 1989). Per hectare the amount of Cl added in 500 mm of irrigation water containing only 200 g Cl m^{-3} is 1000 kg. This is four times more than the amount added in 500 kg KCl ha^{-1}.

2.1.2.3. Rainwater

The importance of airborne Cl, especially in coastal regions, has been recognized for many years (Flowers, 1988). Near the coast, many soils and crops receive a more than adequate supply of Cl from wind-borne sprays of rain and snow (McWilliams and Sealy, 1987). The amount of Cl derived from the atmosphere ranges from 17.6 to 36.0 kg ha^{-1} per year (Reynolds *et al.*, 1997). The salt concentration in the air depends on topography, wind direction and storm distribution (Yaalon, 1963). The concentration in the air decreases exponentially with increasing distance from the shore, becoming uniform at about 50 to 150 km from the shore. Chloride concentrations of 20-50 g m^{-3} have been found in the rainwater close to the shore, diminishing rapidly with distance from the ocean. In inner continental areas the corresponding concentrations are 2-6 g m^{-3}. The quantity of Cl deposited annually is about 175 kg ha^{-1} near the sea, but only 50 kg ha^{-1} at a distance of 6 km from the sea (Yaalon, 1963). Mid-continental areas such as the Great Plains of North America receive less than 1.0 kg Cl ha^{-1} annually through precipitation (Junge, 1963). Atmospheric Cl inputs often increase near heavily industrialized areas where large quantities of coal are burned (Fixen, 1993).

2.2. Potassium and chloride reactions in soil

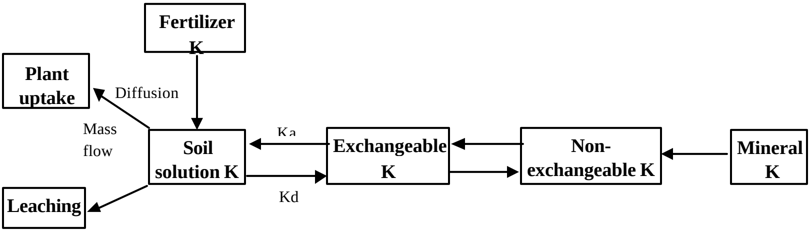
2.2.1. Potassium dynamics in soils

The forms of soil K are as follows (Sparks and Huang, 1985; Mutscher, 1995):

1. Structural K: K contained in crystalline structure either of primary or secondary minerals (K-feldspars, micas and other K-bearing minerals).
2. Fixed K or non exchangeable K: K occupying the internal positions of clay sheets as well as hexagonal cavities of certain minerals, such as illites.
3. Exchangeable K: K bound to a permant negative charge on the surfaces of soil clays and organic matter, thus occupying sites in the soil colloidal complex.
4. K in soil solution: The proportion of the total K in soils held in soil solution is usually very small, and is in equilibrium with exchangeable K.

K in soil solution and exchangeable K are readily taken up by plants, therefore these forms are referred to as *readily available K*. During the course of a growing season, some initially non-exchangeable K may become plant available if uptake by plants exceeds the decrease in the amount of exchangeable K. Thus this K is referred to as *slowly available soil K*. Exchangeable and non exchangeable K are in equilibrium and K transfers readily between these two pools. Both exchangeable and non exchangeable K increase as reserves of K accumulate in soils from application of K in fertilizers and organic manures.

The behavior of K in soil, release, absorption, fixation and leaching, is strongly dependent on the clay content and types of clay minerals present (Mengel and Kirkby, 1987). The various forms of non-exchangeable and exchangeable K are in equilibrium with each other and with the soil solution (Fig. 2.1). Potassium release rates increase as particle size decreases, indicating that in the whole soil, the first fast release of K is primarily from the fine and coarse clay fractions, with a slower rate of release mainly from the coarse clay and fine silt fractions (Cox and Joern, 1997). The reaction rate between soil solution and exchangeable phases of K is strongly dependent on the type of clay minerals present and method employed to measure the kinetics of K exchange (Sparks, 1987). Sparks *et al.* (1980) reported that the reaction coefficient of the adsorption rate (Ka) ranges from about 1 to 20 h^{-1} in soils of predominantly vermiculitic minerals and 81 to 216 h^{-1} in soils of predominantly kaolinite minerals. Desorption of K from *fixed* sites is slower than the adsorption (Feigenbaum and Levy, 1977; Xu *et al.*, 1995), suggesting that hysteresis occurs.



Ka: adsorption rate; Kd: desorption rate

Fig. 2.1. A simple diagramatic representation of the potassium cycle in soils. Modified from Sparks and Huang (1985); Mutscher (1995).

The availability of K is related to its soil solution concentration, soil buffer power and the effective diffusion coefficient (Teo *et al.*, 1994), as well as root growth (Van Rees *et al.*, 1990) and soil bulk density (Dolan *et al.*, 1992; Seiffert *et al.*, 1995). Mc Lean and Watson (1985) suggest that exchangeable K is approximately sufficient for near-maximum yields, when the K content in the soil solution is 5% of the exchangeable K, and approximately 5% of the K requirement of a crop is in solution at one time. In soils with small amounts of micaceous minerals, less preferential bonding to the clay would allow a larger percentage of the K to be in the solution phase.

2.2.2. Sorption competition between potassium, calcium, sodium and magnesium

Some chemical characteristics of K, sodium (Na), magnesium (Mg) and calcium (Ca) in the lithosphere are given in Table 2.2. Among these four cations, the non-hydrated atom K has the largest radius (r=0.133 nm), and in mineral structures the number of oxygen atoms in coordination bonding are large (8 or 12). This suggests that the strength of each K-O bond is relatively weak (Sparks and Huang, 1985). Potassium also has a hydration energy of 142.5 kJ ion^{-1}, indicating that the ability of K to cause soil swelling is small (Helfferich, 1962).

K^+ has larger polarization energy than Na^+, Mg^{2+}, and Ca^{2+}, and is preferred in ion exchange reactions (Sparks, 1987). However, the preference of ion adsorption in soils is influenced by many factors. The adsorption of K is preferred to Ca when soils contain much more exchangeable Ca than exchangeable K (Parfitt, 1992). This preference decreases as more K is added to the soil. Oxidic, allophanic and ultic soils have the least preference for K; brown soils, formed mainly in loess, have the greatest preference, probably due to the presence of many K-selective sites on vermiculite and mica clays in these soils. These findings suggest that Ca, rather than K, is likely to be leached from soils (Parfitt, 1992).

Variable charge soils saturated with hydrogen (H) and aluminium (Al) tend to adsorb K preferentially to Na (Li and Ji, 1992). The distribution of K in the soil solution and on the solid surface does not depend on the level of Na in the solution. The distribution of Na between the two phases depends on the K adsorption ratio (PAR) of the solution (Levy and Feigenbaum, 1996). Gapon selectivity coefficients for Na, calculated separately for each PAR level, also decrease with increasing PAR. Therefore, the Na distribution between the solution and the solid phase in a ternary (K-Na-Ca) system cannot be predicted from the Gapon selectivity coefficient obtained from a binary (Na-Ca) system. The calculated values of standard enthalpy and entropy change indicate that K-Na exchange is endothermic in nature and is accompanied by an increase in the entropy of the system (Singh *et al*., 1993). In smectite-dominant soils there is a preference for Na adsorption than for K. The opposite occurs in soils with equal amounts of smectite and mica in the clay fraction (Singh *et al*., 1993). The specificity for Na adsorption increases with soil organic-C content (Haghnia and Pratt, 1988).

The role of exchangeable Mg in maintaining soil structural stability is still an unresolved issue (Curtin *et al*., 1994, Keren, 1991). The U.S. Salinity Laboratory (Richards, 1954) and Ayers and Westcott (1985) grouped Mg and Ca together as having similar beneficial effects on soil structural stability, and considered them as the same species for evaluation of irrigation water quality.

Table 2.2. Chemical characteristics of K, Na, Mg and Ca in the lithosphere.

Ion	Crystalline radii (nm)	Hydrated radii (nm)	Polarizability (nm^3)	Debye-Huckel parameter (nm)	Coordination No.
K^+	0.133	0.331	0.0876	0.363	8-12
Na^+	0.098	0.358	0.0196	0.397	6.8
Mg^{2+}	0.078	0.428	0.0110	0.502	6.0
Ca^{2+}	0.106	0.412	0.0523	0.473	6.8

Source: Gast (1977), cited from Sparks (1987).

A number of investigators have also assumed that Mg and Ca ions are equally adsorbed (Beckett, 1965; Bresler *et al*., 1982; Van Bladel and Gheyi, 1980). There are also reports suggesting that Mg is less effective than Ca in maintaining soil structure (Rahman and Rowell, 1979; Keren, 1991; Curtin *et al*., 1994) and that soil adsorption of Ca is preferred over that of Mg (Sposito *et al*., 1986). Considerable less soil K is removed from mixed Na-Mg soils than from the Na-Ca soils, when leaching them with solution of total electrolyte concentration less than 100 mM (Levy *et al*., 1988; Curtin *et al*., 1994).

The exchangeable K and Na contents in the soil exchange phase increase as the ratio of Mg to Ca increases (Fig. 2.2). Potassium and Na are more competitive against Mg than against Ca in the soil as Ca adsorption is preferred over that of Mg. The degree of adsorption preference for Na and K over that of Mg in soils, as compared with that of Ca, depends apparently on the nature of the exchangeable complex (Haghnia and Pratt, 1988). The preference for K adsorption in soils with clays dominated by smectite or illite is generally stronger than in vermiculitic soils (Rahman and Rowell, 1979).

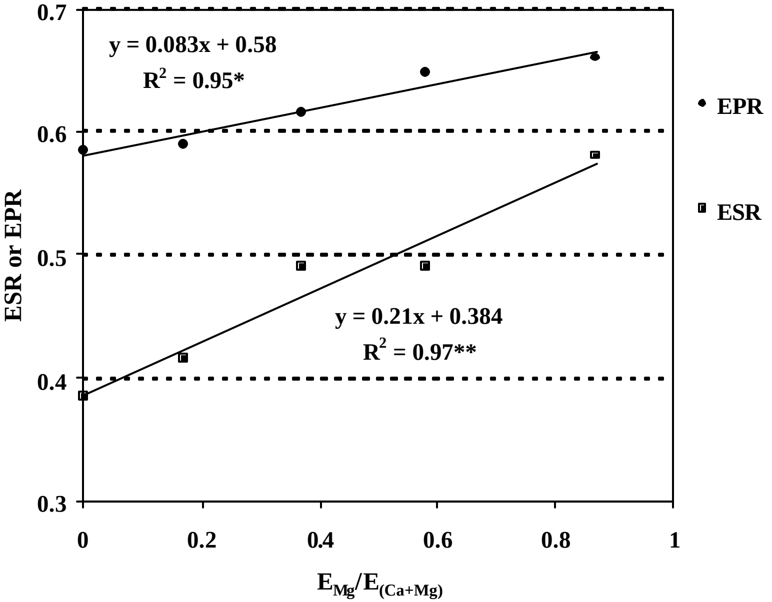


Fig. 2.2. Relationship between the equivalent ratio of exchangeable Na (ESR) or K (EPR) to exchangeable (Ca+Mg) and the Mg fraction of total Ca and Mg [$E_{Mg}/E_{(Ca+Mg)}$] in the exchange phase of a Xerollic Calciorthid mineral soil (Source: Haghnia and Pratt, 1988).

2.2.3. Chloride mobility in soil and reaction with clay surfaces

The Cl anion is not adsorbed on soil particles at neutral and alkaline pH values, and therefore is easily leached. In Cl-deficient soils, the optimal depth for soil sampling to estimate Cl availability to plants depends on the crop's rooting characteristics, as well as the cropping system, soil type, precipitation or frequency of irrigation, and drainage (Fixen, 1993). Huang *et al*. (1995) reported that a large amount of Cl was washed to a depth of 40 to 60 cm in paddy soil after one season of rice growing. Chloride from KCl is mainly found at 30-60 cm depth after one season of corn growing (Parker *et al*., 1985) (Table 2.3). In the North American Great Plains, sampling down to 60 cm is recommended for spring wheat and barley (Fixen *et al*., 1987).

Table 2.3. Effects of adding potassium chloride or sulphate on the distribution of chloride in different depths of a soil profile after one season of corn growing.

Total amount applied			Depth (cm)		
Cl	K	Source	0-15	15-30	30-60
(kg ha^{-1})			Soil Cl (mg kg^{-1})		
0	0	None	22	22	21
85	93	KCl	22	22	34
170	186	KCl	18	30	66
340	372	KCl	29	36	110
0	93	K_2SO_4	24	18	18
0	186	K_2SO_4	21	18	17
0	372	K_2SO_4	17	21	24
340	93	K_2SO_4 + NaCl	23	34	106

Source: Parker *et al*. (1985).

The assumption that Cl ions, like nitrate (NO_3) and perchlorate (ClO_4) ions, are adsorbed on positive sites of clay particles through electrostatic attraction (Borggaard, 1984) is the theoretical basis for the determination of the positive surface charge of soils, as suggested by Schofield (1949). The real behavior of Cl in variable-charge soils differs, however, from that of NO_3 or ClO_4 (Wang and Yu, 1998). The diffusion coefficient of Cl is smaller than that of NO_3, X-ray photoelectron spectroscopic studies show that Cl but not NO_3 reacted with the soil surface (Ji, 1997). The pH values of the suspensions in an HCl- and a HNO_3 -treated system differ in a variable-charge soil, but not in the permanent charge soil (Fig. 2.3.). Therefore, at least for Cl at low pH in variable-charge soils, a specific adsorption is involved. As Cl concentration increases, Cl replaces more OH^- than H_2O

(Wang and Yu, 1998). Release of OH^- ions during specific adsorption of Cl decreases upon removal of the free iron oxides. This hydroxyl ion release, caused by specific adsorption of Cl, increases the soil pH value in chloride solution (Zhang *et al.*, 1989).

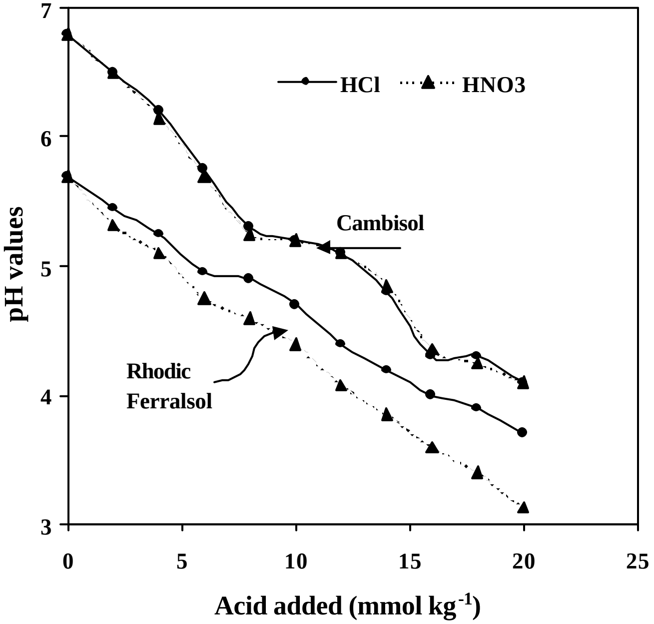


Fig. 2.3. Change in pH for a permanent-charge soil (Cambisol) and for a variable-charge soil (Rhodic Ferralsol) after the addition of different quantities of HCl or HNO_3 (Source: Wang and Yu, 1998).

2.3. Chloride as a nitrification inhibitor

Ammonia fertilizers differ in their rates of nitrification in soil (Meelu *et al.*, 1990). Nitrification of 300 mg NH_4Cl kg^{-1} soil in an acid soil (pH 5.6) at 30°C was only 6% after 21 days as compared to 75% in the case of urea (Hauck, 1984). However, differences in nitrification rates among N sources decreased markedly in an alkaline soil (pH 8.2), except when large amount of N (above 400 mg kg^{-1}) were applied. Whereas all the N added as urea was nitrified in 10 days, it took 35 days for the nitrification of 91% of 300 mg N kg^{-1} as NH_4Cl (Meelu *et al.*, 1990). In another experiment, 80% of $(NH_4)_2SO_4$ was nitrified in 12-18 days, but it was 30-35 days before NH_4Cl was nitrified to the same extent (Babriwara, 1959, cited by Vede Narayanan, 1990). The relative inhibition of the nitrification of NH_4 applied as NH_4Cl was attributed to differences in osmotic potential under different saline conditions or to a direct effect of Cl (Roseberg *et al.*, 1986).

Results of field and laboratory studies indicate that nitrification in acid soils (pH 5.0-5.5) is reduced both by Cl and by the low osmotic potential of the soil solution (Christensen *et al.*, 1986). In soils in which the osmotic potential was increased 4-fold by the addition of NH_4Cl or $(NH_4)_2SO_4$, the nitrification of the $NH_4$was slowed both by Cl and by the decreasing osmotic potential of the soil solution (Table 2.4). Addition of a - 93 kPa solution of Cl salt to the soil resulted in a slower nitrification rate than that obtained with a -680 kPa SO_4 solution. The nitrification essentially stopped when a Cl salt solution of -338 kPa or -680 kPa was added.

The Cl ion functions as a nitrification inhibitor in the soil at pH 5.5 but not at pH 6.6 (Christensen *et al.*, 1986). In slightly acid soils (pH 6.5-7.0), however, the impact of the Cl ion on nitrification is much less. The slower rate of nitrification induced by Cl, particularly in slightly acid soils, might help to increase N use efficiency in rice fields by preventing N losses due to denitrification in the event of flooding.

Table 2.4. Effects of soil pH and osmotic potential of the soil solution after adding either ammonium chloride or ammonium sulphate solutions (100 mg NH_4^+-N kg^{-1} soil) on the rate of nitrification.

Soil	Soil pH	Osmotic potential of added NH_4^+solution[a] (kPa)	Daily nitrification rate (mg NO_3^- -N kg^{-1} soil) NH_4Cl	$(NH_4)_2SO_4$
Woodburn soil	5.3	-93	1.40	2.40
	5.3	-171	0.82	2.12
	5.3	-338	0.10	1.88
	5.3	-680	-0.07	1.75
		LSD (p=0.01)	0.24	
Nekia silty clay loam soil	4.9	-93	5.8	8.8
	5.5	-93	11.2	13.2
	6.2	-93	13.8	14.4
		LSD (p=0.01)	0.48	

[a] Osmotic potentials were changed by adding KCl in NH_4Cl solution or K_2SO_4 in $(NH_4)_2SO_4$ solution.

Based on Christensen *et al*. (1986).

2.4. Soil testing for potassium and chloride

2.4.1. Potassium

2.4.1.1. Extraction of available soil potassium

The different methods of measurement of soil K status were reviewed by Mutscher (1995). Most methods for determining available K exchange it with NH_4, usually 1M NH_4OAc at pH 7 (Haby *et al.*, 1990), although other NH_4 salts are used. Novozamsky and Houba (1987) reported that of the 33 countries and regions they surveyed, 23 use 1M NH_4OAc to determine available soil K. Because water soluble or soil solution K is only a small fraction of the K extracted by this method, it is not measured separately.

There are several other methods of determining readily available soil K for special soil conditions or for various methodological expediencies (Novozamsky and Houba, 1987). In general, the amounts of K extracted are closely similar.

a. The Mehlich No.1 (double acids: 0.05 M HCl in 0.025 M H_2SO_4) method is considered suitable for sandy, acid, low cation exchange capacity (CEC) soils (Fixen and Grove, 1990). Available P can be determined in the extract.

b. The Mehlich No. 2 (a mixture of 0.2 M NH_4OAc, 0.015 M NH_4F, 0.02 M NH_4Cl, and 0.012 M HCl) is used for a wide range of soil conditions (Mehlich, 1978). Its main advantage is that other elements including P and several trace elements are extracted and can be measured in the same extract.

c. The ammonium bicarbonate-DTPA method, developed by Soltanpour and Schwab (1977), extracts exchangeable K plus NO_3 P, and several trace elements. It is used best in alkaline soil conditions (McLean and Watson, 1985).

d. Extraction with 0.01 M $CaCl_2$ solution, which is widely used for determination of soil pH and of available nitrogen, has also been used for readily available K (Novozamsky and Houba, 1987). This method only extracts a proportion of the exchangeable K; the portion depending on the amount of exchangeable K extracted by NH_4OAc.

Schmitz and Pratt (1953) suggested that the reliability of exchangeable K as an index of available K varies with the rate of K release from non-exchangeable forms. In soils where this release rate of K is small, the exchangeable K is the sole supplier and thus reflects plant-available K. When the rate of release of the non-exchangeable K is fast, the exchangeable K level is maintained from the non-exchangeable source, and the exchangeable K reflects both the K release level and the plant available level. In the medium rate of release category between those two extreme conditions, the release rate is considered to be too slow to maintain a large amount of exchangeable K yet is sufficiently fast to be important in supplying K to plants. Therefore, the improve of the correlation between exchangeable K and K uptake by plants could require the inclusion of some estimate of non-exchangeable K.

Under successive intensive cropping condition, soil exchangeable K extracted by NH_4OAc may be reduced to a specific but different minimum value for different soils (Jackson and During, 1979; Sinclair, 1979; Krishnakumari, 1984; Xu *et al.*, 1991). The minimum value is correlated with the supply capacity of non-exchangeable potassium to gramineous and leguminous crops (Xu *et al.*, 1991).

The suitability of different availability indexes of soil K supply status is mainly dependent on crop (Bao, 1989). The exchangeable K can be a good index of soil available K for crops with large requirement for K, such as cotton. K extracted by cold 2 M HNO_3, which generally includes all the exchangeable K and part of non-exchangeable K extracted by boiling 1 M HNO_3, was most closely related with K uptake by gramineous crops like rice, wheat, barley and ryegrass (Xu *et al.*, 1991; Bao and Xu, 1993).

To measure non-exchangeable K, Pratt and Morse (1954) extracted the soil with boiling HNO_3 at 113°C for 25 minutes (including heating plus boiling time). The non-exchangeable K was calculated as the difference between the extracted by boiling HNO_3 and that exchangeable with 1 M NH_4OAc at pH 7.

Other methods used to test the K supply characteristics of soils include extraction with sodium tetraphenylborate ($NaBPh_4$) (Scott and Reed, 1960), cation exchange resin (Feigenbaum *et al.*, 1981) and electro-ultrafiltration (EUF) (Nemeth, 1979). Unlike the boiling HNO_3 method, which is primarily a dissolution process, these extraction methods rely partly on equilibrium conditions between soil K and the extracting solution, and partly on the release of K from the clay lattice.

2.4.1.2. Determination of potassium in the extracts

The classical gravimetric analysis methods for K in solution use tri-sodium cobaltinitrite or sodium tetraphenylborate that form the precipitates of $K_2NaCo(NO_2)_6.H_2O$ or $KBPh_4$. The weight of the precipitate or the turbidity of the solution is used to calculate the K concentration (Chapman and Pratt, 1961; Shi, 1986). Both methods are time-consuming and tedious.

Potassium can also be determined by a potentiometric method using a K-specific, glass ion-electrode. The main disadvantages of this method are the relative large interference by ions in the soil extract and the short life of the electrode (Watson and Isaac, 1990).

The flame emission spectrophotometer (FES) has been the most popular method for the rapid determination of K. The development of new instruments, like the atomic absorption spectrophotometer (AAS) and the inductively coupled plasma emission spectrometry (ICP) have replaced FES in most soil and plant analysis laboratories. Detailed description of the FES, AAS and ICP methodologies can be found in Watson and Isaac (1990).

2.4.2. Chloride

2.4.2.1. Extraction of soil chloride

Soil testing for Cl is generally done for measuring the salt component in saline soils. Because Cl salts are highly water-soluble and Cl is hardly adsorbed, Cl can be extracted with water or weak electrolyte, such as 0.01 M $Ca(NO_3)_2$, 0.5 M K_2SO_4, 100 g l^{-1} HOAc, and CaO-saturated solution. The analytical method for determining Cl in the extractant and the possibility of extracting other elements may influence the choice of extractant. Care should be taken to avoid Cl contamination from dust, water, filter paper, paper bags, perspiration, and many common cleaning agents (Johnson and Fixen, 1990).

Soil testing for Cl is also used to ascertain the Cl status of soils (Fixen *et al*., 1986a; 1986b; Engel *et al.*, 1998), to correlate the values with crop responses. In areas of low Cl, soil testing for this micronutrient may serve as a useful guide for identifying potential responses to Cl fertilization. However, little research has been reported on the use of Cl soil tests, presumably because deficiencies of the element are rare. While suitable extraction and analytical procedures are available for routine testing (Fixen *et al*., 1987), calibration and correlation data are lacking.

2.4.2.2. Determination of chloride in the extracts

The determination of the extracted Cl in the solution can be done by a number of methods, 0.01 M $Ca(NO_3)_2$, 0.5 M K_2SO_4, or a CaO-saturated solution, which relate to the method of analysis by colorimetric, potentiometric, or ion chromatographic procedures, respectively (Fixen *et al.*, 1987).

The classic procedures include gravimetric and two volumetric procedures (Williams, 1984). One of the volumetric procedures is titration with silver nitrate using a chromate indicator (Chapman and Pratt, 1961). In principle, the Cl in the extract first forms a white precipitate of AgCl, then the colorless K_2CrO_4 indicator forms a brown-red precipitate of Ag_2CrO_4 that indicates the end of titration. The amount of Cl in a sample can be obtained by calculating the volume and normality of the standard $AgNO_3$ solution used.

Chloride-specific electrodes can be used to measure the Cl extracted from soils and plant tissues (LaCroix *et al*., 1970; Krieg and Sung, 1977). Both malic and citric acids interfere with the Cl measurement as can other ions, like CN^-, I, Br^-, $S_2O_3^{2-}$, NH_3, OH^-, ClO_4^-, OAc^-, HCO_3^-, SO_4^{2-}, and F, depending on their concentration. Interference from these ionic species is substantial if their concentrations are greater than that of the Cl.

Current analytical methods for determining soil Cl extracts are: a colorimetric determination using mercury thiocyanate (Adriano and Doner, 1982; Schumacher and Fixen, 1989), and a silver nitrate titrant and a Cl ion selective electrode (e.g. Orion 96-17B) (Watson and Isaac, 1990). The second method, a coulometric amperometric titration, is accurate and precise for determining Cl extracted from soil and plant tissue samples. In the chloride titrator, a constant direct current is passed between a pair of Ag generator electrodes (Ag wire) in the coulometric circuit, which release Ag ions into the titration solution at a constant rate, and react with Cl in the sample to form a precipitate. When all the Cl has been precipitated, the increasing flow of Ag^+ through the Ag electrodes, stops the timer. The timer runs concurrently with the generation of Ag^+. Since the rate of Ag^+ generation is constant, the amount of Cl precipitated is proportional to the elapsed time (Watson and Isaac, 1990).

The main advantage of the potentiometric titration is the sensitivity and the lack of interfering species (although sulfide and iron will interfere at very high concentrations). The primary disadvantage is with high Cl concentrations when it can take considerable time to reach the end-point (Watson and Isaac, 1990).

References

Adriano, D.C. and Doner, H.E. (1982): Bromine, chlorine and fluorine. *In*: "Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties" (A.L. Page, ed.) pp. 449-483. ASA/SSSA, Madison, WI.

Ayers, R.S. and Westcott, D.W. (1985): Water quality for agriculture. Food and Agricultural Organization of the United Nations, Irrigation and Drainage Paper **29**, Rev. 1.

Bao, S.D. (1989): Potassium diagnosis and potash fertilization of cotton. *J. Nanjing Agri. Univ*. (Chinese). **12,** 131-138.

Bao, S.D. and Xu, G.H. (1993): Study on contemporary and residual effects of potassium fertilizer under rotation of wheat and rice. *J. Nanjing Agri. Univ*. (Chinese). **16,** 43-48.

Beckett, P.H.T. (1965): The cation-exchange equilibria of Ca and Mg. *Soil Sci*. **100,** 118-123.

Bertsch, P.M. and Thomas. G.W. (1985): Potassium Status of Temperate Region Soils. *In:* "Potassium in Agriculture" (R.E. Munson, ed.). pp. 131-162. ASA/CSSA/SSSA, Madison, WI.

Borggaard, O.K. (1984): Influences of iron oxides on non-specific anion (chloride) adsorption by soils. *J. Soil Sci.* **35,** 71-78.

Bresler, E., Mc Neal, B.L. and Carter, D.L. (1982): Saline and Sodic Soils. Springer Verlag, New York.

Chapman, H.D. and Pratt, P.F. (1961): Methods of Analysis for Soils, Plants and Waters. Univ. California Div. Agr. Sci., Riverside, CA.

Christensen, N.W., Roseberg, R.J., Brett, M. and Jackson, T.L. (1986): Chloride inhibition of nitrification as related to take-all disease of wheat. *In:* "Special Bulletin on Chloride and Crop Production" (T.L. Jackson, ed.), No. 2, pp. 22-39. Potash & Phosphate Institute, Atlanta, Georgia.

Cox, A.E. and Joern, B.C. (1997): Release kinetics of non-exchangeable potassium in soils using sodium tetraphenylboron. *Soil Sci.* **162**, 588-598.

Curtin, D., Steppuhn, H. and Selles, F. (1994): Effects of magnesium on cation selectivity and structural stability of sodic soils. *Soil Sci. Soc. Am. J.* **58,** 730-737.

Dolan, M.S., Dowdy, R.H., Voorhees, W.B., Johnson, J.F. and Bidwell Schrader, A.M. (1992): Corn phosphorus and potassium uptake in response to soil compaction. *Agron. J.* **84**, 639-642.

Engel, R.E., Bruckner, P.L. and Eckhoff, J. (1998): Critical tissue concentration and chloride requirements for wheat. *Soil Sci. Soc. Am. J.* **62,** 401-405.

Feigenbaum, S. and Levy, R. (1977): Potassium release in some saline soils of Israel. *Geoderma* **19,** 159-169.

Feigenbaum, S., Edelstein, R. and Shainberg, I. (1981): Release rate of potassium and structural cations from micas to ion exchangers in dilute solutions. *Soil Sci. Soc. Am. J.* **45,** 501-506.

Fixen, P.E. (1993): Crop responses to chloride. *Adv. Agron.* **50**, 107-150.

Fixen, P.E., Buchenau, G.W., Gelderman, R.H., Schumacher, T.E., Gerwing, J.R., Cholick, F.A. and Farber, B.G. (1986a): Influence of soil and applied chloride on several wheat parameters. *Agron. J.* **78**, 736-740.

Fixen, P.E., Gelderman, R.H., Gerwing, J.R. and Cholick, F.A. (1986b): Response of spring wheat, barley and oats to chloride in potassium chloride fertilizers. *Agron. J.* **78,** 664-668.

Fixen, P.E., Gelderman, R.H., Gerwing, J.R. and Farber, B.G. (1987): Calibration and implementation of a soil Cl test. *J. Fert. Issues* **4,** 91-97.

Fixen, P.E. and Grove, J.H. (1990): Testing soils for phosphorus. *In:* "Soil Testing and Plant Analysis" (R.L. Westerman, ed.). pp. 141-180. SSSA, Madison, WI.

Flowers, T.J. (1988): Chloride as a nutrient and as an osmoticum. *Adv. Plant Nutr.* **3,** 55-78.

Goos, R.J. (1987): Chloride fertilization: the basics. *Crops Soils* **39,** 12-13.

Haby, V.A., Russelle, M.P. and Skogley, E.O. (1990): Testing soils for potassium, calcium and magnesium. *In:* "Soil Testing and Plant Analysis" (R.L. Westerman, ed.). pp. 181-221. SSSA, Madison, WI.

Haghnia, G.H. and Pratt, P.F. (1988): Effect of exchangeable magnesium on the accumulation of sodium and potassium in soils. *Soil Sci.* **145,** 432-436.

Hauck, R.D. (1984): Nitrogen in Crop Production. pp. 507-519. ASA, Madison, WI.

Helfferich, F. (1962): Ion Exchange. Mc Graw-Hill Book Co., New York.

Huang, P.M. (1977): Feldspars, olivines, pyroxenes and amphiboles. *In:* "Minerals in Soil Environments" (J.B. Dixon and S.B. Weed, eds.). pp. 553-602. SSSA, Madison, WI.

Huang, Y., Rao, Y.P. and Liao T.J. (1995): Migration of chloride in soil and plant. *J. Southwest Agric. Univ*. (Chinese) **17**, 259-263.

Jackson, B.L.J. and During, C. (1979): Studies of slowly available potassium in soils of New Zealand. I. Effects of leaching, temperature and potassium depletion on the equilibrium concentration of potassium in solution. *Plant Soil* **51,** 197-204.

Jackson, M.L. (1964): Chemical Composition of Soils. *In:* "Chemistry of the Soil" (F.E. Bear, ed.). pp. 71-141. Van Nostrand Reinhold, New York.

Ji, G.L. (1997): Electrostatic adsorption of anions. *In:* "Chemistry of Variable Charge Soils" (Yu T.R., ed.), pp. 112-139. Oxford University Press, New York.

Johnson, G.V. and Fixen, P.E. (1990): Testing soils for sulfur, boron, molybdenum and chlorine. *In:* "Soil Testing and Plant Analysis" (R.L. Westerman, ed.), 3rd Ed., Vol. 3, pp. 265-273. SSSA Book Series, Madison, WI.

Junge, C.E. (1963): Air Chemistry and Radioactivity. Academic Press, New York.

Keren, R. (1991): Specific effect of magnesium on soil erosion and water infiltration. *Soil. Sci. Soc. Am. J.* **55,** 783-787.

Krieg, D.R. and Sung, D. (1977): Interference in chloride determination using the specific ion electrode. *Commun. Soil Sci. Plant Anal.* **8,** 109-114.

Krishnakumari, M. (1984): Studies on potassium release in an Inceptisol soil the minimum level of exchangeable potassium. *Plant Soil* **79,** 3-10.

LaCroix, R.L., Keeney, D.R. and Walsh, L.M. (1970): Potentiometric titration of chloride in plant tissue extracts using the chloride ion electrode. *Commun. Soil Sci. Plant Anal.* **1,** 1-6.

Levy, G.J. and Feigenbaum, S. (1996): The distribution of potassium and sodium between the solution and the solid phase in a ternary (K-Na-Ca) system. *Aust. J. Soil Res.* **34,** 749-754.

Levy, G.J., Van der Watt, H.V.H. and Du Plessis, H.M. (1988): Effect of sodium-magnesium and sodium-calcium systems on soil hydraulic conductivity and infiltration. *Soil Sci.* **146,** 303-310.

Li, H.Y. and Ji, G.L. (1992): Adsorption of potassium and sodium ions by variable charge soils. *Pedosphere* **2**, 245-254.

McLean, E.O. and Watson, M.E. (1985): Soil Measurements of plant available potassium. *In:* "Potassium in Agriculture" (R.D. Munson, ed.). pp. 277-308. ASA/CSSA/SSSA, Madison, WI.

McWilliams, E.L. and Sealy, R.L. (1987): Atmospheric chloride: its implication for foliar fruit disorders. Fact Sheet HS-140. Institute of Food and Agricultural Sciences, University of Florida.

Meelu, O.P., Yadvinder, S. and Bijay, S. (1990): Relative efficiency of ammonium chloride under different agro-climatic conditions – a review. *Fertilizer News (*Fertilizer Association of India), New Delhi.

Mehlich, A. (1978): New extractant for soil test evaluation of P, K, Mg, Ca, Na, Mn and Zn. *Commun. Soil Sci. Plant Anal.* **9,** 477-492.

Mengel, K. and Kirkby, E.A. (1987): Principles of Plant Nutrition. 4th Ed. International Potash Institute, Basel, Switzerland.

Mutscher, H. (1995): Measurement and Assessment of Soil Potassium. IPI Research Topics 4. International Potash Institute, Basel, Switzerland.

Nemeth, K. (1978): Limitation of present soil test interpretations for K and suggestions for modification. A. European experience. *In:* "Potassium in Soils and Crops". pp. 97-111. Potash Research Institute of India, New Delhi.

Novozamsky, I. and Houba, V.J.G. (1987): Critical evaluation of soil testing methods for K. *In:* "Methodology in Soil-K Research". pp. 177-197. International Potash Institute, Basel, Switzerland.

Pan, J.R., Liu, B.J., Zhang, X.Z. and Wen, X.F. (1991a): Study of residual effects of chloride fertilizers using tracer chloride isotope. *J. Nucl. Agric. Sci.* (Chinese) **12**, 182-184.

Parfitt, R.L. (1992): Potassium-calcium exchange in some New Zealand soils. *Aust. J. Soil Res.* **30**, 145-158.

Parker, M.B., Gaines, T.P. and Gascho, G.J. (1985): Chloride effects on corn. *Commun. Soil Sci. Plant Anal.* **16**, 1319-1333.

Pratt, P.F. and Morse, H.H. (1954): Potassium release from exchangeable and non-exchangeable forms in Ohio soils. *Ohio Agric. Exp. Stn. Res. Bull.* No. 747.

Rahman, W.A. and Rowell, D.L. (1979): The influence of magnesium in saline and sodic soils: a specific effect or a problem of cation exchange. *J. Soil Sci.* **30,** 535-546.

Reynolds, B.D., Fowler, R., Smith, I. and Hall, J.R. (1997): Atmospheric inputs and catchment solute fluxes for major ions in five Welsh upland catchments. *J. Hydrol.* **194,** 305–329.

Richards, L.A. (ed.) (1954): Diagnosis and Improvement of Saline and Alkali Soils. U.S. Department of Agriculture, Agriculture Handbook No. 60. U.S. Government Printing Office, Washington DC.

Roseberg, R.J., Christensen, N.W. and Jackson, T.L. (1986): Chloride, soil solution osmotic potential and soil pH effects on nitrification. *Soil Sci. Soc. Am. J*. **50,** 941-945.

Schmitz, G.W. and Pratt, P.F. (1953): Exchangeable and non-exchangeable potassium as indexes to yield increases and potassium absorption by corn in the greenhouse. *Soil Sci.* **76,** 345-353.

Schofield, R.K. (1949): Effect of pH on electric charge carried by clay particles. *J. Soil Sci.* **1,** 1-8.

Schumacher, W.K. and Fixen, P.E. (1989): Residual effects of chloride application in a corn-wheat rotation. *Soil Sci. Soc. Am. J.* **53**, 1742-1747.

Scott, A.D. and Reed, M.G. (1960): Determination of the precipitated potassium in sodium tetraphenylboron-micaceous mineral systems. *Soil Sci. Soc. Am. Proc.* **24,** 326-327.

Seiffert, S., Kaselowsky, J., Jungk, A. and Claassen, N. (1995): Observed and calculated potassium uptake by maize as affected by soil water content and bulk density. *Agron. J.* **87**, 1070-1077.

Sheldrick, W.F. (1985): World potassium reserves. *In:* "Potassium in Agriculture" (R.D. Munson, ed.). pp. 3-29. ASA/CSSA/SSSA, Madison, WI.

Shi, R.H. (ed.) (1986): Soil and Agro-Chemistry Analysis. 2nd ed. Chinese Agricultural Press, Beijing, China.

Sinclair, A.H. (1979): Availability of potassium to ryegrass from Scottish soils. *J. Soil Sci.* **30,** 757-783.

Singh, B., Srivastava, P.C. and Agnihotri, A.K. (1993): Potassium-sodium exchange equilibria in some irrigated soils of Rajasthan, India. *J. Potassium Research.* **9**, 189-195.

Soltanpour, P.N. and Schwab, A.P. (1977): A new soil test for simultaneous extraction of macro-and micro-nutrients in alkaline soils. *Commu. Soil Sci. Plant Anal.* **8,** 195-207.

Sparks, D.L. (1987): Potassium dynamics in soils. *Adv. Soil Sci.* **6,** 1-64.

Sparks, D.L. and Huang, P.M. (1985): Physical chemistry of soil potassium. *In:* "Potassium in Agriculture" (R.D. Munson, ed.). ASA/CSSA/SSSA, Madison, WI.

Sparks, D.L., Zelazny, L.W. and Martens, D.C. (1980): Kinetics of potassium desorption in soil using miscible displacement. *Soil Sci. Soc. Am. J.* **44,** 37-40.

Sposito, G., LeVesque, C.S. and Hesterberg, D. (1986): Calcium-magnesium exchange on illite in the presence of adsorbed sodium. *Soil Sci. Soc. Am. J.* **50,** 905-909.

Teo, Y.H., Beyrouty, C.A., Norman, R.J. and Gbur, E.E. (1994): Nutrient supplying capacity of a paddy rice soil. *J. Plant Nutr.* **17**, 1983-2000.

Van Bladel, R. and Gheyi, H.R. (1980): Thermodynamic study of calcium-sodium and calcium magnesium exchange in calcareous soils Montmorillonite clays. *Soil Sci. Soc. Am. J.* **44,** 938-942.

Vede Narayanan, P.N. (1990): Handbook of Ammonium Chloride Fertilizer. McMillan, India.

Wang, J.H. and Yu, T.R. (1998): Release of hydroxyl ions during specific adsorption of chloride by variable-charge soils. *Z. Pflanzenernähr. Bodenk*. **161,** 109-113.

Watson, M.E. and Isaac, R.A. (1990): Analytical instruments for soil and plant analysis. *In:* "Soil Testing and Plant Analysis" (R.L. Westerman, ed.), 3rd edition, pp. 691-740. SSSA, Madison, WI.

Williams, S. (1984): Official Methods of Analysis of the Association of Official Analytical Chemists. Assoc. Off. Anal. Chem., Arlington, VA.

Xie, J.C. and Hasegawa, M. (1985): Organic and inorganic sources of potassium in intensive cropping system: experiences in the People's Republic of China and Japan. *In:* "Potassium in Agriculture" (R.D. Munson, ed.). pp. 1177-1200. ASA/CSSA/SSSA, Madison, WI.

Xu, G.H., Bao, S.D. and Shi, R.H. (1991): Utilization of soil interlayer potassium by graminous and leguminous crops. *J. Nanjing Agri. Univ.* (Chinese). **14,** 47-52.

Xu, G.H., Bao, S.D. and Shi, R.H. (1995): Characteristics of natural release and fixation of interlayer potassium in soils exhausted by cropping. *Soils* (Chinese). **27,** 182-185.

Yaalon, D.H. (1963): The origin and accumulation of salts in groundwater and in soils in Israel. *Bull. Res. Counc. Israel,* **11G**, 105-131.

Yin, M.J., Sun, J.J. and Liu, C.S. (1989): Contents and distribution of chloride and effects of irrigation water of different chloride levels on crops. *Soil Fert.* (Chinese) **1,** 3-7.

Zhang, X.N., Zhang, G.Y., Zhao, A.Z. and Yu, T.R. (1989): Surface electro-chemical properties of B horizon of a Rhodic Ferralsol, China. *Geoderma* **44,** 275-286.